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FeMnSb: A HALF-METALLIC FERRIMAGNET

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We have determined the magnetic and crystallographic properties of intermetallic compounds of the type $\text{Ni}_{1-x}\text{Fe}_x\text{MnSb}$, using standard X-ray diffraction techniques, magnetic measurements and ^{57}Fe Mössbauer spectroscopy. These materials were found to have the cubic MgAgAs structure (C1_b) for concentrations $x < 0.1$ and the CoMnSb structure related to C1_b for concentrations $0.7 < x < 0.9$. Lattice constants, saturation moments and Curie temperatures were found to vary smoothly with x , making it possible to derive values for all these physical constants of FeMnSb by extrapolation. Calculation of the electronic band structure of FeMnSb revealed that this compound can be regarded as a novel type of material. Like the half-metallic ferromagnet NiMnSb , the compound FeMnSb has a band gap near the Fermi energy in the band structure of the minority spin electrons. This band gap stabilizes an antiparallel coupling between the Mn and Fe moment, so that one may characterize this compound as a half-metallic ferrimagnet.

1. Introduction

The compound NiMnSb crystallizes in the cubic MgAgAs structure (C1_b structure). The electronic band structure of this compound can be characterized as metallic for one spin direction and at the same time as semiconducting for the other spin direction [1,2]. In the present study we report on the magnetic and crystallographic properties of compounds of the series $\text{Ni}_{1-x}\text{Fe}_x\text{MnSb}$. The interest in these materials has resulted from features of the electronic band structure of CoMnSb . This latter compound, too, proved to be a half-metallic ferromagnet like NiMnSb , the only difference between the two compounds being the lower Mn moment in the CoMnSb , whereas the Co moment is slightly higher than the Ni moment in NiMnSb [3]. The results obtained on CoMnSb showed that

the total number of valence electrons is less critical in establishing the energy gap in the band structure of the minority spin electrons than it was initially thought to be. This suggests the possibility that it is relatively unimportant which 3d atom is chosen for X in XMnSb , the electronic structure of the minority spin electrons (including the gap) being stable enough to deal with any changes of this kind by an appropriate adaptation of the corresponding magnetic moments. To test this hypothesis we have made band structure calculations for FeMnSb which will be presented in this paper. Unfortunately a search of the literature indicated that a ternary compound of the composition FeMnSb does not exist, which we were able to confirm. We therefore looked for other means of providing an appropriate experimental basis for the band structure calculations of FeMnSb . To

this end we studied the series $\text{Ni}_{1-x}\text{Fe}_x\text{MnSb}$ and found it to be suitable for determining the magnetic and crystallographic properties of the non-existing compound FeMnSb by extrapolation to high Fe concentrations.

2. Experimental

Various samples of the series $\text{Ni}_{1-x}\text{Fe}_x\text{MnSb}$ were prepared by arc melting, followed by vacuum annealing at 800°C for 3 weeks. After annealing the samples were quenched in water and investigated by X-ray diffraction. Diffraction diagrams were recorded with $\text{CuK}\alpha$ radiation on a Philips powder diffractometer equipped with a graphite crystal monochromator.

Magnetic measurements were made in the range 4.2–900 K with magnetic field strengths up to 1440 kA/m by means of the Faraday method. The Curie temperatures were determined from the temperature of the magnetization (σ) measured in low fields ($H \leq 80$ kA/m) by plotting σ^2 versus T and extrapolating the linear part to $\sigma^2 = 0$.

The ^{57}Fe Mössbauer spectra were obtained by means of a standard constant-acceleration type spectrometer equipped with a ^{57}Co –Rh source.

3. Experimental results

X-ray diffraction of $\text{Ni}_{1-x}\text{Fe}_x\text{MnSb}$ showed that the cubic Cl_b structure is found only for small Fe concentrations. For $x \geq 0.1$ the compounds were found to occur in two different modifications having the cubic Cl_b structure and the cubic structure found in CoMnSb, respectively. In the latter structure type the situation differs from that found in NiMnSb in so far as the Co atoms not only occupy the 4(a) site at 0, 0, 0 in the Cl_b structure but partially occupy also the (empty) 4(b) site at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$. There is a minor displacement of the Co and Sb atoms from the ideal positions in the Cl_b type and the unit cell dimensions of CoMnSb have doubled with respect to the Cl_b type [4]. This doubling of the unit cell leads to the occurrence of superstructure lines in the X-ray diffraction diagram in addition to the

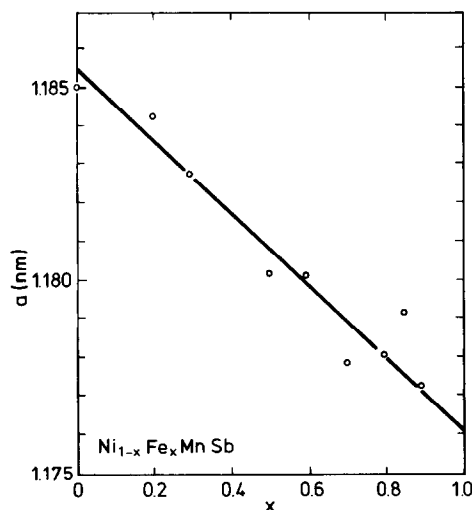


Fig. 1. Concentration dependence of the lattice constants (a) for $\text{Ni}_{1-x}\text{Fe}_x\text{MnSb}$. The lattice constants correspond to the doubled unit cell dimension of the Cl_b structure.

(much stronger) lines present in the Cl_b as well as in the CoMnSb structure. The lattice constants of the compounds investigated are plotted as a function of composition in fig. 1. For the purposes of comparison we have indexed the lines in the diffractogram of the Ni-rich compounds on the basis of the doubled unit cell. Intensity calculations for $\text{Ni}_{1-x}\text{Fe}_x\text{MnSb}$ based on the CoMnSb structure showed that the intensity of the superstructure lines is very low. For this reason it was not possible to obtain an estimate of the relative amounts of both modifications in $\text{Ni}_{1-x}\text{Fe}_x\text{MnSb}$ (Cl_b type and CoMnSb type).

In the X-ray diagrams of compounds of intermediate concentrations we observed some line broadening which blurred the α_1 – α_2 splitting of the high-angle diffraction lines. This might indicate the occurrence of concentration fluctuations or the presence of two (or more) crystallographic phases differing slightly in lattice constant.

More relevant in this respect are the results of magnetic measurements. The temperature dependence of the magnetization of various $\text{Ni}_{1-x}\text{Fe}_x\text{MnSb}$ compounds is compared in fig. 2. It can be inferred from the curves shown that most of the samples are composed of two magnetic phases (A and B) having Curie temperatures near $T_c^A = 730$

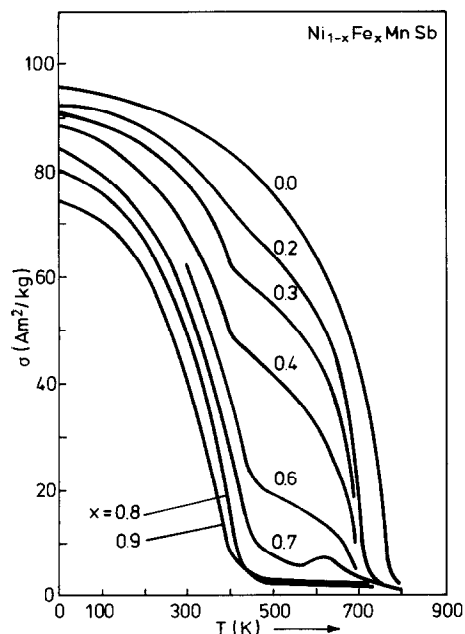


Fig. 2. Temperature dependence of the magnetization (σ) of various $\text{Ni}_{1-x}\text{Fe}_x\text{MnSb}$ samples ($H = 7200$ kA/m).

K and $T_c^B = 350$ K, respectively. With increasing Fe concentration phase B increases at the expense of phase A. The values of the saturation moment measured for each of the samples at 4.2 K are

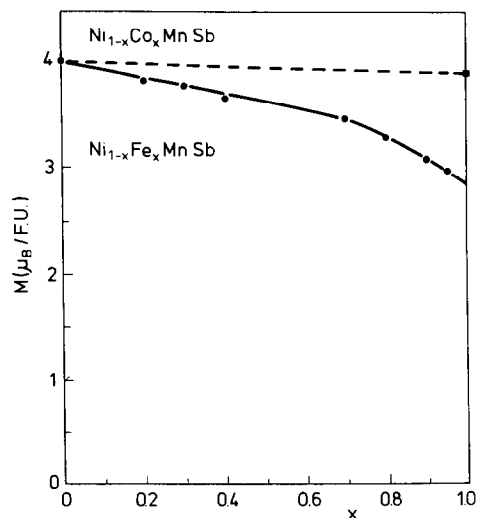


Fig. 3. Concentration dependence of the saturation moment M (in Bohr magnetons per formula unit) of various $\text{Ni}_{1-x}\text{Fe}_x\text{MnSb}$ samples. The broken line corresponds to $\text{Ni}_{1-x}\text{Co}_x\text{MnSb}$.

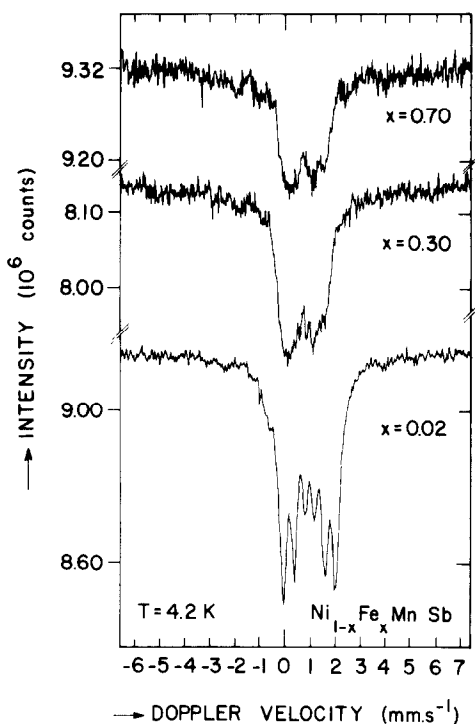


Fig. 4. ^{57}Fe Mössbauer spectra at 4.2 K of various $\text{Ni}_{1-x}\text{Fe}_x\text{MnSb}$ samples.

plotted as a function of concentration in fig. 3.

Results of ^{57}Fe Mössbauer spectroscopy at 4.2 K are shown in fig. 4. For preparing the alloy with $x = 0.02$ we used iron metal 90% enriched with the ^{57}Fe isotope. The spectrum of the latter alloy is relatively sharp. Larger Fe concentrations lead to some line broadening the hyperfine splitting remaining approximately the same.

Although results for the sample with $x = 0.5$ are not included in fig. 2, it can be inferred from the results shown that the phases A and B are present in this sample in about equal proportions. We studied the temperature dependence of the Mössbauer spectra of this sample in more detail. A magnetic hyperfine splitting similar to that of the spectra shown in fig. 4 was observed only at temperatures well below $T_c^B \approx 350$ K. Near room temperature the magnetic splitting becomes strongly reduced and at temperatures in excess of T_c^B only a singlet was observed. This includes the temperature range between T_c^A and T_c^B .

4. Interpretation of the experimental results

From the results described in the previous section it follows that most of the $\text{Ni}_{1-x}\text{Fe}_x\text{MnSb}$ samples gave rise to the occurrence of two different phases. Phase A is of the Cl_b type and has the higher Curie temperature ($T_c \approx 730$ K), phase B is of the CoMnSb type and has the lower Curie temperature ($T_c \approx 370$ K). In phase A the Ni(Fe) atoms occupy only the 4(a) site whereas in phase B there is a partial occupation of both the 4(a) and the 4(b) site. The 4(a) and 4(b) sites have in common that their nearest neighbour configuration is the same. In both cases it consists of two intertwined tetrahedrons of 4 Mn atoms and 4 Sb atoms, respectively. This similarity in nearest neighbour configuration is probably the reason why the hyperfine field of the Fe atoms does not change with concentration. The next nearest neighbours associated with the Ni(Fe) atoms at the 4(a) and 4(c) sites consist of Ni(Fe) atoms, and here one may expect differences between the 4(a) and 4(c) sites with respect to the total number of next nearest neighbours but also with respect to the types of atoms (Ni or Fe). We believe that these differences in next nearest neighbour coordination are the origin of the line broadening observed in the ^{57}Fe Mössbauer spectra obtained on samples with larger Fe concentration than in the sample with $x = 0.02$ shown in fig. 4.

The magnetic measurements showed that in the intermediate concentration range two different phases are present which both become magnetically ordered (below) $T_c^A \approx 730$ K and $T_c^B \approx 370$ K, respectively). The observation that the hyperfine splitting disappears above about 370 K suggests that the Fe atoms are accommodated almost exclusively in the B phase. In an alternative explanation of the Mössbauer spectra one might consider the possibility that a substantial part of the Fe atoms occurs in the A phase but that the corresponding hyperfine splitting is very small or zero, owing to a zero Fe moment or to a cancellation between core polarization and transferred hyperfine field. However, in this case the relatively strong singlet near zero velocity observed above T_c^B is also expected to be dominant below this temperature, which apparently is not the case (see fig. 4).

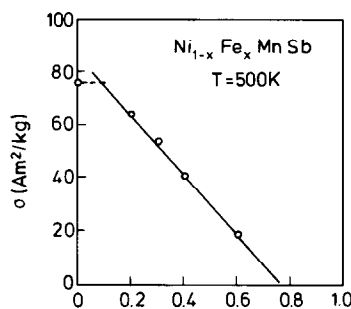


Fig. 5. Concentration dependence of the magnetization σ measured at $T = 500$ K ($H = 7200$ kA/m).

Combining the results of X-ray diffraction, magnetic measurements and ^{57}Fe Mössbauer spectroscopy one may further specify the system $\text{Ni}_{1-x}\text{Fe}_x\text{MnSb}$ as consisting of four regions: For low Fe concentrations $0 \leq x < 0.1$ the Cl_b structure is stable. The disordered Cl_b structure (CoMnSb type) exists in the range $0.75 < x \leq 0.95$. In the intermediate concentration range one has a mixture of both types, the relative amount of the latter increasing with x . The decreasing saturation moment (M) in the range $0.1 < x < 0.75$ (see fig. 3) has then to be interpreted as being the result of a decreasing amount of the Cl_b phase with a relatively high value of M in favour of the disordered Cl_b phase with a somewhat smaller value of M . At $T = 500$ K the situation is more simple since only the Cl_b phase A is magnetically ordered. At this temperature the decreasing amount of this phase is seen in fig 5 to lead to a linear decrease of the magnetization. Finally, for Fe concentrations higher than $x = 0.95$ phases of different composi-

Table 1

Lattice constants (a), Curie temperatures (T_c), experimental saturation moments (M_{exp}) and calculated saturation moments for NiMnSb, CoMnSb and FeMnSb. The value in parenthesis given for FeMnSb represents the saturation moment for the ferrimagnetic configuration (for more details see text)

Compound	a (nm)	T_c (K)	M_{exp} (μ_B /f.u.)	M_{calc} (μ_B /f.u.)
NiMnSb	1.1850 *	730	4.08	4.00
CoMnSb	1.1750	490	3.93	3.00
FeMnSb	1.1762	370	2.7	2.00 (5.09)

* Doubled unit cell.

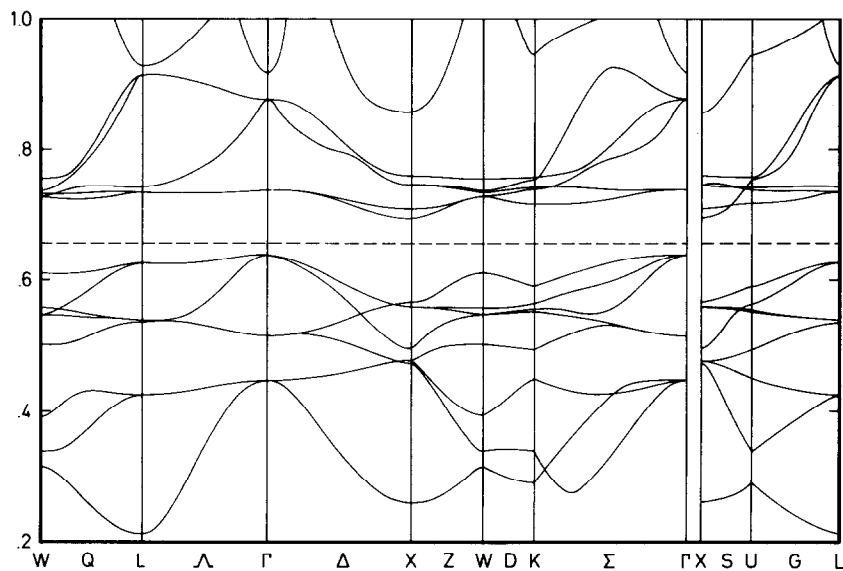


Fig. 6. Electronic band structure for minority spin electrons in FeMnSb.

tion and crystal structures not related to the $C1_b$ structure occur.

It is somewhat unfortunate that, owing to the influence of competing phases of different composition, the ternary compound FeMnSb does not exist. However by extrapolating the experimental

results obtained in the previous section one may easily derive the magnetic properties which this compound would possess if it existed. These properties are compared with those of NiMnSb and CoMnSb in table 1.

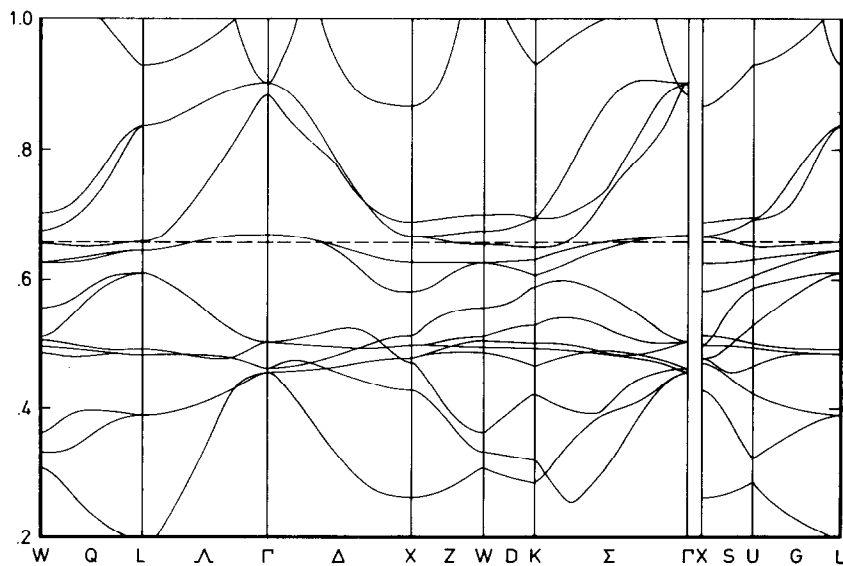


Fig. 7. Electronic band structure for majority spin electrons in FeMnSb.

5. Band structure calculations

Band structure calculations for the compounds NiMnSb and CoMnSb have previously been reported [1–3]. Both band structures were calculated on the basis of the $C1_b$ structure type, although some disorder of the Co atoms occurs in CoMnSb [4]. The same procedure will be adopted here for FeMnSb, in the hope that the basic features calculated for the ordered $C1_b$ structure type will hold to a large extent for the disordered structure as well. The calculations were performed by means of the self-consistent augmented spherical (ASW) method of Williams, Kübler and Gelatt [5], including scalar relativistic effects as described by

Methfessel and Kübler [6]. The occupied 4(b) positions at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ in the $C1_b$ type crystal structure were treated as atoms with zero nuclear charge. From the results of the calculations it was inferred that the use of the quasi-empirically determined lattice constant for FeMnSb leads to only a modest pressure. For this reason no attempts were made to minimize the total energy as a function of the lattice constant.

The band structures for the majority and minority spin directions are shown in figs. 6 and 7, respectively. The energy dependence of the density of states is given in fig. 8.

6. Discussion

Inspection of the band structures for the majority and minority spin directions in FeMnSb (figs. 6 and 7) shows that this material is not a common magnetic metal, since electron bands intersect the Fermi level only in the majority spin directions. The spectacular feature present in NiMnSb and CoMnSb, where the minority band structures have semiconducting gaps straddling the Fermi surface, is present in FeMnSb as well. Nevertheless the band structure of FeMnSb possesses a novel feature which does not allow this material to be characterized as a half-metallic ferromagnet. This novel feature is apparent from fig. 8 after comparison of the local density of states of both spin directions for Mn and Fe. It can be derived from the results shown that Mn carries a magnetic moment of about $3\mu_B$, whereas Fe carries a moment of about $1\mu_B$. But these moments have an antiparallel orientation, which means that FeMnSb is a half-metallic ferrimagnet rather than a half-metallic ferromagnet.

In order to investigate the nature of the magnetic ordering a calculation was also performed for the ferromagnetic state. This was realized by applying an external magnetic field in the calculation, big enough to accomplish the metal-magnetic transition to the ferromagnetic state and subsequently reducing this field slowly enough to ensure that the system remains in its metastable ferromagnetic state. The calculation gave a magnetic moment of $5.09\mu_B$, it was a normal magnetic

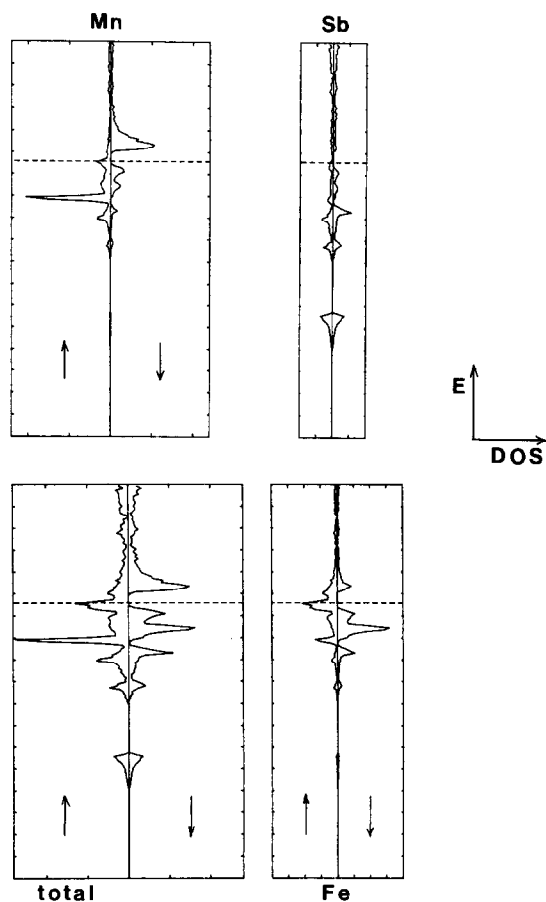


Fig. 8. Density of states derived from band structure calculations for FeMnSb.

state for both spin-directions without gaps. The state densities at the Fermi-level were 18 and 31 states/Ry f.u. for majority and minority spin-directions, respectively. The absence of energy gaps in the ferromagnetic state implies that the half-metallic behaviour of the ferromagnetic state is directly responsible for the stability of the ferrimagnetic state: The energy gain of the gap in the minority spin direction is lost for other spin-configurations. This constitutes a new contribution to the exchange coupling on top of (but not in conflict with) known contribution to the (super) exchange.

The results of the band structure calculations are only roughly confirmed by the experimental results. We will first discuss the Fe moments. From the ^{57}Fe Mössbauer spectra we concluded that the effective hyperfine field at the Fe nuclei is equal to about 1 T. The ratios used to convert hyperfine fields into the corresponding Fe moments range from $0.9 \text{ T}/\mu_{\text{B}}$ in Fe-Sn compounds to $1.4 \text{ T}/\mu_{\text{B}}$ in compounds of Fe with elements of the third row of the Periodic Table [7,8]. This would mean that the Fe moment in FeMnSb is of the order of $1\mu_{\text{B}}$, which is in satisfactory agreement with the results of the band structure calculations. However, comparison of the total moment derived experimentally for FeMnSb with the total moment derived from the band structure calculations (table 1) shows that the latter is substantially lower than the former.

Band structure calculations made by Kübler for CoMnSb (assuming the Cl_b structure) showed that the Mn atoms carry a moment equal to about $3\mu_{\text{B}}$, while the moment of the Co atoms is rather small [3]. This means that the saturation moment in the series $\text{Ni}_{1-x}\text{Co}_x\text{MnSb}$ is expected to decrease continuously from about $4\mu_{\text{B}}$ ($x=0$) to about $3\mu_{\text{B}}$ ($x=1$). Experimentally one observes hardly any decrease (broken line in fig. 3). Apparently the moment calculated for Mn is somewhat too low. We attribute this discrepancy to the difference in crystal structure between NiMnSb and CoMnSb, recalling that the simple cubic Cl_b structure is observed experimentally only in the former compound. In view of the similarity in crystal structure between CoMnSb and FeMnSb it may be suspected that the discrepancy between

the observed and the calculated Mn moment may then also be present in FeMnSb. Taking this for granted, one expects that the total moment in FeMnSb will be about $1\mu_{\text{B}}$ lower than the total moment in CoMnSb owing to the ferrimagnetic arrangement between Fe and Mn moments. This difference in total moment is indeed reflected in the experimental as well as in the calculated values listed in table 1. Neutron diffraction measurements needed to verify the ferrimagnetic nature of the Fe-rich compounds of the series $\text{Ni}_{1-x}\text{Fe}_x\text{MnSb}$ are planned in the near future.

6. Concluding remarks

We have shown that a ternary compound of the composition FeMnSb having a structure related to Heusler alloys does not exist. In the system $\text{Ni}_{1-x}\text{Fe}_x\text{MnSb}$ such compounds do exist up to Fe concentrations $x \leq 0.95$. The physical constants describing the magnetic and crystallographic properties of the fictitious compound FeMnSb were obtained with a fairly high degree of accuracy by extrapolation. Band structure calculations made for FeMnSb revealed this compound to be a novel type of material which may be described as a half-metallic ferrimagnet. The ferrimagnetic coupling between Fe and Mn moments is stabilized by the occurrence of the energy gap in the band structure of the minority spin electrons.

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